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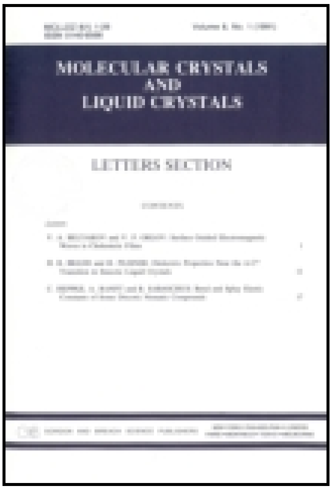

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Efficient Bilayer Electrodes for Photosensitive Organic Heterostructure

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Efficient Bilayer Electrodes for Photosensitive Organic Heterostructure

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The possibility of increasing the photosensitivity of organic heterostructures by using the bilayer transparent ITO electrodes with organic conducting polymer polyaniline, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) complex (PEDOT:PSS) and CuI has been verified experimentally. Photosensitive n*-type organic semiconductor N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide (MPP) and p-type pentacene were chosen as components of these heterostructures. Usage of ITO/PEDOT:PSS bilayer electrodes leads to increasing the photovoltaic sensitivity of these heterostructures by 2–3 orders and by 1–2 orders when using CuI due to decreasing the recombination of excitons and increasing the potential barrier heights on the interface between the organic semiconductor and layers of PEDOT:PSS and CuI.*

Keywords Organic heterostructures; bilayer electrodes; PEDOT:PSS; CuI; N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide; pentacene

1. Introduction

Nowadays, the photoelectric processes in organic heterostructures (OHS) and polymer composites are widely been studying for cheep flexible organic solar cells [1–2]. The efficiency of these organic solar cells (OSC) slowly but confidently increases substantially due to new photosensitive materials and improvements in the technology of organic layer deposition [3–4]. At the present time, the processes on the interface between a photovoltaically active layer and electrodes are studied not enough, though they substantially influence the stability [5, 6], recombination rates of excitons and charge carriers [7], series resistance [8], and, therefore, the short-circuit photocurrent and the efficiency factor of OSC. It is difficult to obtain simultaneously good adhesion, stability, low recombination rate, and desired potential barrier height with the use of the anode and the cathode made only from the same material. The ITO electrodes have a good adhesion to glass and quartz substrates and are stable. But, on the interface between a photosensitive organic semiconductor (OS) and the electrode, the significant concentration of uncontrollable impurities, which work as the traps for excitons and charge carriers, is formed [6, 7]. On the other hand, the frequently used layers of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) complex and CuI

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have bad adhesion to glass substrates, but good adhesion to layers of ITO and OS. It should be noted that the layers of PEDOT:PSS were already used in some structures, which differ by the materials of electrodes, photosensitive component material,s and technologies of top electrode deposition. Therefore, it is difficult to estimate the contribution of a PEDOT:PSS layer into increasing the efficiency of elements [3, 8]. The aim of this paper is to study the influence of bilayer electrodes on the increase of the photosensitivity of the heterostructures with the layers of OS.

2. Experimental

The layers of PEDOT:PSS have been made as follows. The ITO-glass substrate was successively washed by ulrasonication in acetone and then in 2-propanol and pure water followed by the treatment with boiling H_2O_2 and dried in air. These substrates were then spin-coated by a PEDOT:PSS layer from a 1.3 wt% water dispersion of PEDOT:PSS (Aldrich) at 2000 rpm for 20 s followed by baking at 120°C for 30 min under argon.

Thin polyaniline films were deposited on the cleaned and degreased surface of ITO-electrodes by electrochemical polymerization from a 0.1 M aniline solution in 0.5 M sulphuric acid at T = 293 K. The synthesis was carried out in a specially designed quartz cell, where the working electrode has form of a disc 12 mm in diameter, which was fixed by platinum clips. A Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The current density was $i = 0.05$–$0.1\ \mathrm{mA/cm^2}$, and the potential of the working electrode was $E = 0.78$–0.82 V [10].

Photosensitive organic semiconductors of the *n*-type, N,N′-dimethyl-3,4,9,10-perylenetetracarboxylic acid diimide (MPP) [11], and of the *p*-type, pentacene (Pn) [12], were chosen as components for the fabrication of photosensitive heterostructures.

Heterostructures have been prepared by vacuum evaporation of Pn and MPP layers on the substrates heated to $T_s = 370$ K, where the highest photovoltage, V_s, was observed [6–7, 9, 11–13]. The deposition technology of CuI layers was described in [11].

The thickness of OS layers was controlled by a quartz oscillator during the deposition process. After the deposition, it was confirmed by AFM and by measurements of the optical density D at the wavelengths $\lambda = 750$ nm for polyaniline layers and $\lambda = 520$ nm for Pn layers, where the absorption coefficient does not depend on the substrate temperature T_s [10, 15].

Absorption spectra were measured by a double ray spectrophotometer "Hitachi" or "CA-46" at T = 293 K.

Photovoltage measurements were carried out by the contactless means at a modulated illumination [16]. The power of monochromatic light was controlled by a calibrated radiometer PPTN-02 on the basis of a silicon photodiode.

3. Results and Discussion

3.1 Surface Morphology

The topology of obtained ITO, PEDOT:PSS and OS films on the glass substrates was studied by an AFM "NanoScope IIIa". The software from the PSI Company was used for the data accumulation and treatment such as filtering, smoothing, and statistical analysis of the obtained pictures.

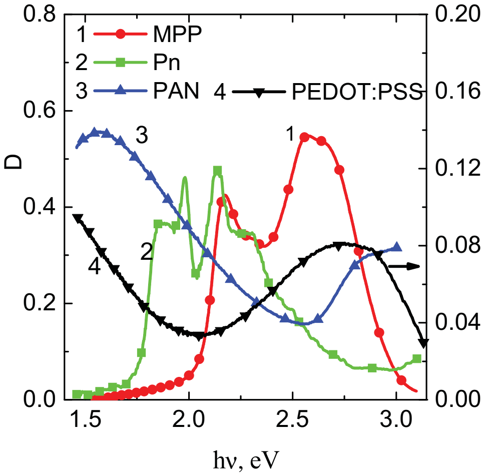

Figure 1. Absorption spectra of the components of heterostructures: MPP (1), Pn (2), PAN (3), and PEDOT:PSS (4).

The AFM study of the surface of electrochemically obtained polyaniline films shows that PAN films are fine-graded with a crystallite size of ∼100 nm and a small number of aggregates on the surface with sizes 0.5–1.0 μm. The maximal value of heights is ∼1.1 μm and their root mean square (RMS) deviation is 136 nm. The similar RMS values were also obtained for MPP and Pn films prepared by vacuum evaporation [9–14]. Deposition of PEDOT:PSS films by spin-coating leads to a significant smoothing of the surface of substrates with ITO; i.e., PEDOT:PSS films passivate the defect regions with the leakage of carriers.

3.2 Absorption Spectra

The absorption spectra of PAN, PEDOT:PSS, Pn, and MPP are shown in Fig. 1. It is well seen that the use of PAN/MPP bilayer structures leads to a significant widening of the spectral region of sun light absorption as a result of the absorption in the polymer films.

At the same time, the potential on the electrode-film/OS interface must be changed, because the photoelectron work function of PAN (4.4 eV [16]) and PEDOT:PSS (5.2 eV [3]) differs from the work function of ITO (4.7 eV). The increase of the sun light absorption as a result of decreasing the reflectance from the structures with PEDOT:PSS films on ITO is negligible (Fig. 2.).

3.3 Photovoltaic Properties of PEDOT:PSS/OS and PAN/OS Heterostructures

The photovoltages of studied structures differ much (3–4 orders) from one another. The photovoltages of ITO/PEDOT:PSS and ITO/PAN are small; therefore, it was impossible to measure their spectral dependences. For the correct comparison of the photovoltages of different structures, the measurements under modulated illumination from light diodes with different photon energies and from different substrate sides were carried out. They are shown in Table 1. The photovoltages of ITO/PAN/OS and ITO/PEDOT:PSS/OS structures

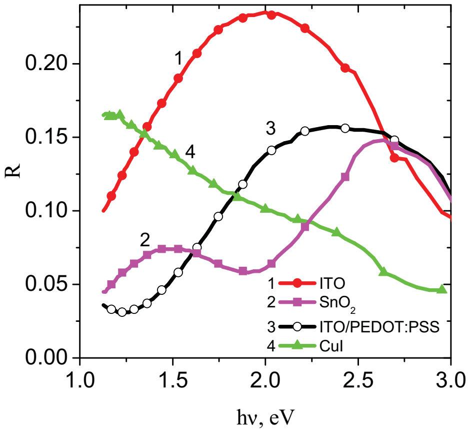

Figure 2. Reflection spectra of the layers: ITO (1), ITO/ PEDOT:PSS (2), SnO_2 (3), ITO/CuI (4) at the illumination through the glass substrate.

are significantly larger than the photovoltage of the ITO/OS structure and by a few orders larger than that in the case of ITO/polymer structures.

Meanwhile, increasing the photovoltage is almost one order larger for structures with a PEDOT:PSS layer than that for those with a PAN layer relative to that of the ITO/Pn structure.

This is the evidence of the fact that the significantly larger potential difference is formed at the polymer/OS interface than that at the ITO/OS interface. Consequently, the larger built-in electric field appears, which enhances the separation efficiency of photogenerated charge carriers. The potentials difference is larger in the structures with PEDOT:PSS layer.

The relationship of photovoltages of these structures depends on the excitation energy. It can be connected with different nature of excited states and with changes in the recombination efficiency of charge carriers. To estimate the contribution of these processes, the measurements of photovoltage spectral dependences were carried out. They are shown in Figs. 3–5.

It is seen from Fig. 3 that the photovoltage for the ITO/PAN/MPP heterostructure is maximal in the interval of 2.5–2.8 eV, i.e., in the spectral range of excitation of two types

Table 1. Photovoltages of structures on the basis of PAN and PEDOT:PSS with Pn and MPP films under the illumination of the front side of the substrate by light diodes

Excitation energy, eV Structures,	1.32	1.90	2.18	2.64
	Photovoltage, V/W			
ITO/PEDOT:PSS	0.8	20	21	9
ITO/Pn	0.2	1060	257	750
ITO/PAN /Pn	0.4	2000	640	160
ITO/ PEDOT:PSS /Pn	2	50000	21400	6430
ITO/PAN	0.2	83	385	160
ITO/MPP	0.42	73	940	375
ITO/ PEDOT:PSS /MPP	8	470	4700	4820

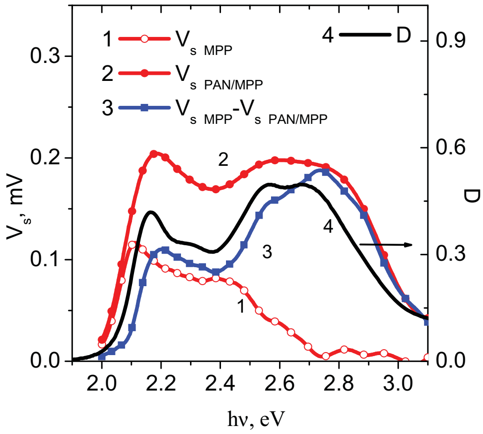

Figure 3. Spectral dependences of the photovoltage V_s of the structures: ITO/MPP (1), ITO/PAN/MPP(2) and their difference (3). The spectral dependency of MPP layer optical density D (4).

of CT excitons in the MPP layer, and it is about 1.5 times larger than that in the range of excitation of Frenkel excitons [10, 17]. Meanwhile, the increase is larger at the excitation of excitons with an energy of 2.7 eV. It can be caused by a more effective separation of excitons with charge transfer by the internal field, which gives the major contribution to the charge carrier photogeneration in the films of MPP in this region [10].

The similar increase of photovoltages is also observed for ITO/PAN/Pn structures (Fig. 4.). The maximal increase is in the interval of 2.4–2.7 eV, i.e., in the range of the

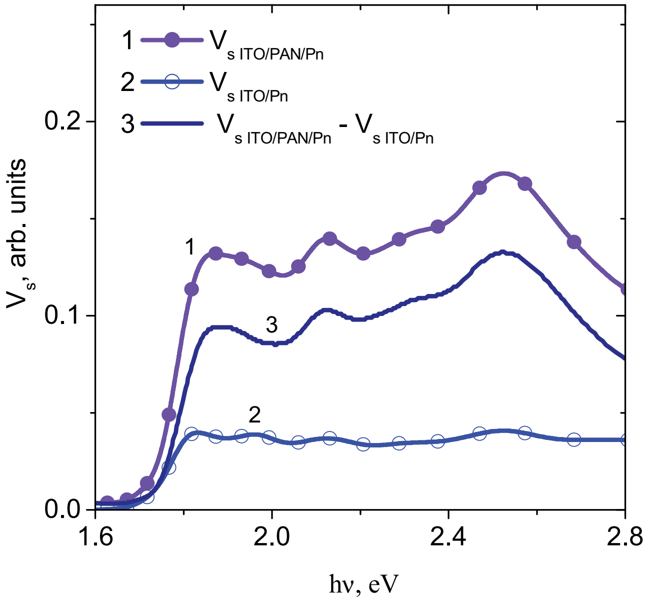

Figure 4. Spectral dependences of the photovoltage V_s of the structures: ITO/PAN/Pn (1), ITO/Pn (2), and their difference (3) under the illumination through the ITO electrode.

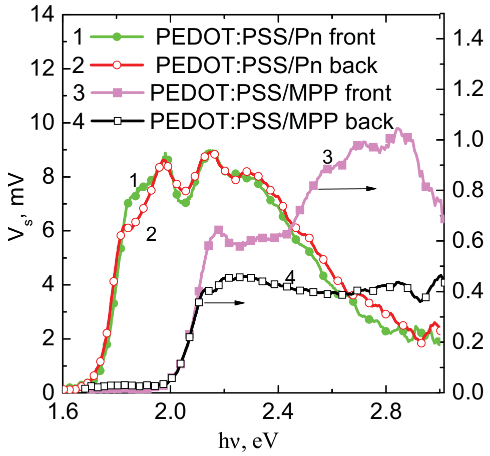

Figure 5. Spectral dependences of the photovoltage V_s of the heterostructures: PEDOT:PSS/Pn (1,2) and PEDOT:PSS/MPP (3,4) under the illumination through the layer of Pn (1), MPP (3), and PEDOT:PSS (2,4).

autoionization of higher excited states (hν > 2.2 eV). This process occurs also through the CT states, and the photogeneration efficiency of charge carriers in the interval of 2.4–2.7 eV is more strongly dependent on the electric field strength than in the excitation range of Frenkel excitons (1.9–2.1 eV). That is, the larger increase of photovoltages is caused in this case by the more effective separation of CT-states [10, 14, 17] in the presence of the intermediate layer.

The measurements of the photovoltage spectral dependences of ITO/PEDOT:PSS/Pn and ITO/ PEDOT:PSS /MPP heterostructures showed that their photovoltages more strongly increase after the formation of a heterostructure in comparison with the photovoltage of ITO/Pn and ITO/MPP structures and are maximal in the range of the strong absorption of Pn and MPP layers (Fig. 5.).

The maximal photovoltagein PEDOT:PSS/Pn structures is 40–60 times larger than in PAN/Pn structures. For PEDOT:PSS/MPP heterostructures, it is 5 times larger than that in PAN/MPP heterostructures. The peculiarity of the PEDOT:PSS/Pn heterostructure is the independence of the photovoltage of the direction of illumination, i.e., the charge carrier photogeneration process covers the whole bulk of a Pn film, and all carriers reach the interface as a result of the large exciton diffusion length in this film (200 nm) [7, 12]. In MPP films, the diffusion length of excited excitons is much less (30 nm [11, 13]); i.e., it is less than the film thickness (100 nm). Therefore, a part of photogenerated CT excitons recombines and does not reach the space charge region. As a result, the dependence of the photovoltage on the illumination direction appears (Fig. 5, curves 3, 4). This is consistent with that the photovoltage is larger under illumination through the substrate, because the internal electric field is concentrated near the PEDOT:PSS/MPP interface.

3.4 Photovoltaic Properties of MPP/CuI Heterostructures

The spectral dependences of photovoltages of the ITO/MPP structures prepared at T_s = 370 K before and after the zCuI layer deposition under illumination of the front side of MPP or CuI are presented in Fig. 6. The deposition of a CuI layer on the MPP surface, i.e. the heterostructure formation, leads to a significant increase of the photovoltage V_s, which

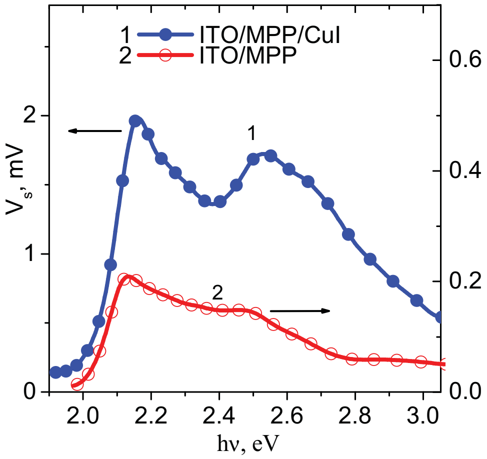

Figure 6. Spectral dependences of the photovoltage V_s of the heterostructures PEDOT:PSS/Pn (1, 2) and PEDOT:PSS/MPP (3, 4) under the illumination through the layer of Pn (1), MPP (3), and PEDOT:PSS (2, 4).

is larger at the excitation of CT excitons (2.5–2.7 eV) than at the excitation of Frenkel ones (2.1–2.3 eV). This increase can be caused by increasing the band bending at the MPP/CuI interface and decreasing the surface recombination rate of charge carriers.

The dependence of the photovoltage, V_s, on the absorption coefficient, α, under weak illumination must be linear, and the angle of the slope is proportional to the band bending at the interface. The dependence $V_s(\alpha)$ becomes nonlinear and tends to the saturation [20–22], when the rate of surface recombination of charge carriers increases.

The dependences $V_s(\alpha)$ are shown in Fig. 7 in the region of the absorption band with maximum at 2.15 eV. It is seen that, for MPP films, the deviation from the linearity with the approach to a saturation mode is observed (Fig. 7, curve 2). This indicates the existence of a high surface recombination rate of excitons and charge carriers near the front side

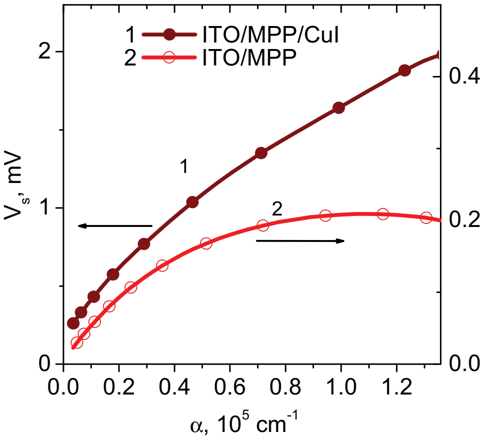

Figure 7. Dependences of the photovoltage V_s on the absorption coefficient for ITO/MPP/CuI (1) and ITO/MPP (2) heterostructures prepared at $T_s = 370$ K under the illumination of the front side of CuI (1) or MPP (2).

of MPP films. After the CuI layer deposition, the dependence $V_S(\alpha)$ becomes closer to a linear one with increasing the slope angle (Fig. 7, curve 1). So, the deposition of a CuI thin layer on the MPP surface leads to a significant band bending increase at the interface and to decreasing the surface recombination rate of excitons and charge carriers. This can be the evidence of a significant decrease of the concentration of surface trap centers and the recombination rate of charge carriers at the vacuum exhaustion of adsorbed air molecules on the MPP surface (before the CuI deposition). Consequently, the band bending of the barrier type is formed on the interface between MPP (n-type) and CuI (p-type) causing a low capture and a low recombination rate of charge carriers.

4. Conclusions

It is established that the use of bilayer ITO/PEDOT:PSS and ITO/CuI electrodes leads to the increase of the photovoltaic sensitivity of the structures by 2–3 and 1–2 orders, respectively. The comparison of the spectral dependences of the photovoltaic properties of the structures with and without intermediate PEDOT:PSS layer shows that they are caused by a decrease of the recombination rate of excitons and charge carriers and an increase of the potential barrier height at the interface between MPP and the layer of PEDOT:PSS or CuI. In addition, the photovoltaic sensitivity increase is larger at the excitation of excitons with charge transfer than that in the case of Frenkel excitons that can be caused by the more effective separation of CT excitons in the built-in electric field at the interface between PEDOT:PSS and MPP. The measurements of the photovoltaic properties of other structures show that the increase of the photovoltaic sensitivity is observed also for ITO/PEDOT:PSS/Pn and ITO/PAN/MPP structures and the value of increase depends on the material of the intermediate layer and on the organic semiconductor.

So, the use of the bilayer electrodes transparent in the visible spectral region (ITO/PEDOT:PSS and ITO/PAN) allows one to optimize not only the uniformity and the work function of electrodes, but also to increase the photovoltaic sensitivity of their heterostructures with the films of organic semiconductors as a consequence of the decrease of the recombination efficiency of excitons at the interface and a change in the potential barrier height. The highest increase of the photovoltage is observed in ITO/PEDOT:PSS/MPP structures at the excitation of excitons with charge carriers.

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